

L170,858

# PATENT SPECIFICATION

NO DRAWINGS

L170,858



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## COMPLETE SPECIFICATION

### Tobacco Substitute and Method of Making the Same

We, PHILIP MORRIS INCORPORATED, a Corporation organized and existing under the laws of the State of Virginia, United States of America, of 100 Park Avenue, New York, New York 10017, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a product for smoking in the form of a cigarette, cigar or cigarillo and also to a burnable sheet for use in such a product, as a tobacco substitute.

The nature of smoking products is such that the manufacture of a tobacco substitute is an extremely difficult operation. The subtleties of smoking and of producing a product which will be satisfactory to a smoker, *inter alia* from a taste and flavour aspect, make synthesis of such a product difficult. Thus, while many attempts have been made to prepare tobacco substitutes, none has resulted in the development of a satisfactory tobacco substitute.

The biological requirements for the growth of a tobacco plant are very different from the chemical and physical requirements for the generation of a smoke which is desirable to a smoker. Thus, there are often constituents in tobacco which result in a less desirable smoke from a smoker's viewpoint and which tend to affect adversely the character of smoke from tobacco products. Thus, tobacco, being a natural product, contains some constituents which would be better omitted, were the user of the tobacco given his choice. In addition, tobacco varies greatly from crop to crop, and even from leaf to leaf, in both its chemical constitution and its physical structure. It would clearly be most advantageous if a smoking product could be designed in such a manner that it has all of the desirable properties of tobacco, and none

of the undesirable properties. Such a synthetic product or tobacco substitute would make it possible to omit from the formulation those constituents which have an adverse affect, either biologically or organoleptically, and to permit the incorporation in the smoking product of those constituents which have been demonstrated to be desirable in smoke.

In accordance with the present invention, a tobacco substitute has been developed which can provide the satisfaction and smoking pleasure of natural tobacco and which, at the same time, can be free of undesirable properties often encountered in natural tobacco. Furthermore, the present invention provides a smoking product which is completely uniform and can be produced under controlled conditions.

According to the present invention, there is provided a product for smoking in the form of a cigarette, cigar or cigarillo which contains no tobacco plant parts and which comprises a mixture of from 5 to 95% by weight of a film-forming ingredient which is an acid gum having an acid value exceeding 30 mg. of potassium hydroxide per gram of gum, and from 5 to 90% by weight of a mineral ingredient, the balance, if any, consisting of compatible ingredients. The essential ingredients are thus (1) a film-forming ingredient and (2) a mineral ingredient. These two ingredients will be discussed in more detail below.

(1) The film-forming ingredient. The film-forming ingredient is preferably a pectinaceous material but may also be, for example, an alginic material. The film-forming ingredient must have an acid gum having an acid value in excess of 30 milligrams of KOH per gram of gum. One class of substances, the calcium-magnesium-potassium-sodium salts of the polyuronic acids, constitutes about one-third of the structural carbohydrate of leaf tobacco, and provides, in

[Price 4s. 6d.]

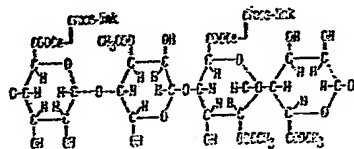
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combined form, the necessary mineral support for the "coal". Representatives of this class include acidic pectins and pectates that are available from tobacco, pectin from citrus fruits, alginic acid, polyuronic acids, salts of these acids, synthetic esters of alginic acid, esters of pectic acids, and other pectins that will form films. Pectins of all degrees of methylation can be used. Even blends of high and low molecular weight pectic materials may be used. Most preferably, a pectinic material is employed which is derived from tobacco plant parts containing pectins having alkaline earth metal cross-links and is obtained by:

1. Contacting the tobacco plant parts with a reagent to destroy the alkaline earth metal cross-links therein;
2. At least partially releasing the resulting tobacco pectins from the interstices of the treated tobacco plant parts; and
3. Recovering the tobacco pectins.

Such a material provides a particularly desirable film-forming ingredient. Some of the methods for producing such tobacco pectins will be described below. In the description which follows the term "pectin substances" (for convenience, unless otherwise specified, the term "pectins" will hereinafter be employed as meaning "pectin substances") will mean those substances which are found in many plant products. They consist essentially of partially methylated galacturonic acids joined in long chains.

The pectins found in tobacco plants contain acetyl groups and differ from commercially available pectins found in other plants, including sugar beet pectins and citrus and fruit pectins. Tobacco protopectins are uniquely insoluble in hot water and, in many instances, the pectic chains are particularly stable in alkaline solutions as compared with protopectins from many other sources and comprise mainly water-insoluble pectins (protopectins) consisting of the calcium and magnesium salts of partially esterified and slightly acetylated polymers of galacturonic acid. The divalent calcium and/or magnesium atoms act as cross-links between acid chains, thus making the polymers water-insoluble. As an illustration, the structure of the calcium salt of a polymer of galacturonic acid can be represented as follows:



Although pectins have long been known as constituents of plant tissue, it has been found

extremely difficult to separate pectins from the remainder of plant compositions and to obtain them as homogeneous compositions. The recovery of pectins from tobacco is even more difficult than the recovery of pectins from other plants.

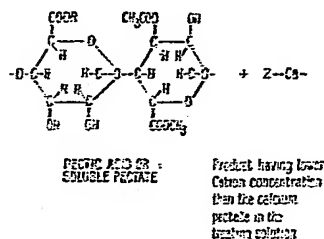
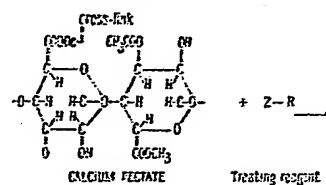
The tobacco parts which can be employed in making the film-forming ingredient include tobacco leaves, stems and stalks, and mixtures of these, in sheet, flake or particulate form. Preferably, the parts are ground, cut or otherwise prepared in a form which presents a large surface area. The portions of the plant comprising the stems or midribs (often referred to as tobacco petioles) are preferred. Tobacco stalks contain lesser amounts of pectinaceous materials but can also be employed.

In the first step of the process, tobacco pectins are liberated from pectinaceous materials in tobacco by reacting the pectinaceous materials with a reagent which is reactive with the calcium (and/or magnesium) contained in them to form a product having a lower calcium ion and/or magnesium ion, concentration in the treating solution than the naturally occurring calcium (or magnesium) pectate. By concentration is meant mean concentration of activity as set forth in Glasstone, "Textbook of Physical Chemistry", 2nd Edition, page 945, D. V. Nostrand Company, Inc.

The reaction may be generally represented by Equation I, which illustrates the reaction of one type of tobacco protopectin (a calcium salt of a polymer of galacturonic acid) having calcium cross-links. In the equation, R may be hydrogen, in which case the product is pectic acid, or R may be a monovalent inorganic cation, such as sodium, potassium or ammonium.

Equation I is as follows:

Equation I



In one embodiment of this process, the

reagent, which can be and preferably is, in aqueous solution, acts by forming a precipitate with the calcium or magnesium, in which case it can be a water-soluble monovalent metal salt of the formula  $M_nX$  wherein M is a monovalent inorganic cation,  $n$  is 1, 2 or 3, and X is an anion which may be monovalent or polyvalent, such that the calcium salt of the formula  $Ca_pX_q$ , in which  $p$  and  $q$  are integers corresponding to the functionality of X is essential insoluble in the treating solution. Monovalent cations which are effective include the alkali metals such as sodium potassium and lithium, and ammonium and substituted ammonium ions  $(NR_4)^+$ , wherein R is aryl or alkyl. The anion portion of the molecule may be, for example,  $CO_3^{2-}$ ,  $PO_4^{3-}$ ,  $HPO_4^{2-}$ , or  $H_2PO_4^-$ . For example, the compound  $M_nX$  could be sodium carbonate,  $Na_2CO_3$ , since sodium is a monovalent inorganic cation and calcium carbonate is essentially water-insoluble. Other examples include the orthophosphates, metaphosphates, and carbonates of sodium, potassium, lithium and ammonium. In the case of the orthophosphates, the anion portion of the molecule may be either  $PO_4^{3-}$ ,  $HPO_4^{2-}$  or  $H_2PO_4^-$ . Specifically, for example, when ammonium orthophosphate is used, the precipitate is calcium and/or magnesium ammonium phosphate. The pH of this reaction mixture should generally be between 5.8 and 10 and the temperature should preferably be between 25°C. and 135°C., for a period of from 1 minute to 24 hours. Specific examples of precipitating agents which may be employed include sodium carbonate, potassium carbonate, lithium carbonate, ammonium orthophosphate, ammonium acid phosphate, and sodium orthophosphate.

In a second embodiment of this process, the reagent acts by sequestering the calcium or magnesium, thereby removing the calcium or magnesium atoms by forming a soluble complex therewith. Suitable reagents of this type include any sequestering agent which will form a complex or chelate with the calcium or magnesium thereby removing them and making them unavailable for re-cross-linking with the pectin. Such sequestering agents include ethylenediaminetetraacetic acid, alkali metal polymetaphosphates such as tetra-metaphosphates, hexametaphosphates and trimetaphosphates, pyrophosphates and tripolyphosphates, such as sodium hexametaphosphate, tetrasodium pyrophosphate and pentasodium tripolyphosphate. Many naturally occurring amines and peptides are also effective as sequestering agents for calcium and/or magnesium. Representative examples include alanine, aspartic acid, glycine, glycyglycine, glutamic acid, serine, tyrosine and di-iodo-L-tyrosine. Amino acids that are effective as chelating solubilizing

agents include betaalanine, N,N-diacetic acid; amino barbituric acid, N,N-diacetic acid; 2-amino-benzoic acid, N,N-diacetic acid; beta-aminoethyl-phosphonic acid; N,N-diacetic acid; beta-aminoethylsulfonic acid and N,N-diacetic acid. The pH of the reaction mixture should generally be between 4 and 10 and the temperature should preferably be between 0°C. and 145°C., for a period of from 1 minute to 24 hours.

A reagent may also function partially as a precipitating reagent, in accordance with the first embodiment and partially as a sequestering agent, in accordance with the second embodiment. Such a reagent, for example, is DAP (diammonium monohydrogen orthophosphate).

In a third embodiment of this process, the reagent is an acid which produces insoluble free pectic acid and soluble calcium and magnesium salts. Suitable such acids include inorganic acids, such as hydrochloric acid, phosphoric acid and sulphuric acid and similar acids which will form calcium and magnesium salts under the following conditions. The acid may generally be employed as 0.25 N to 5.0 N solutions, but is preferably employed as 0.5 N to 1.0 N solutions. The exact dilution and amount to be employed will vary with the particular acid which is used, it only being necessary that sufficient acid be present to convert the calcium and magnesium present in the tobacco being treated to the corresponding calcium and magnesium salts. The acid treatment is preferably conducted at a temperature of from -1°C. to 55°C. The acid treatment comprises reacting the tobacco parts with the acid until the resulting mixture has a pH of from 1.0 to 2.5. Preferably the pH is brought to from 1.0 to 1.7, the most desirable pH being between 1.15 and 1.55. This treatment will generally be conducted from 10 minutes to 24 hours, depending in part on the size of the tobacco particles.

Preferably, the resulting mixture is then washed with water. This water-wash step is preferably conducted at a temperature of from 15 to 35°C. and, preferably, distilled water is employed. When this wash step is employed, sufficient water should be used to remove the calcium and magnesium salts of the acids, thus, there should be at least 2 volumes of water per volume of the mixture resulting from the acid treatment. The wash water is separated from the tobacco by any suitable means, for example by conducting the wash in a centrifuge, filter press or Buchner funnel.

The mixture resulting from the acid treatment, and preferably after the water wash described above, is then suitably brought to a pH of from 2.7 to 10.5, by the addition of an alkaline material. Suitable alkaline

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100

105

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115

120

125

130

Revised  
PIF

Washed  
diammonium  
PIF

materials include alkali metal, such as sodium, potassium and lithium and ammonium hydroxide, and alkali metal salts of weak acids, such as sodium bicarbonate, sodium carbonate, sodium phosphate to convert the pectic acid to a soluble form. The alkaline material may be any water-soluble compound containing a monovalent inorganic cation which is capable of producing hydroxide ions when dissolved in water. Preferably the alkaline treatment is conducted until the pH of the resulting mixture has a value of from 4.5 to 5.5. The temperature of this step may be from  $-1^{\circ}\text{C}.$  to  $45^{\circ}\text{C}.$ , but is preferably from  $15^{\circ}$  to  $35^{\circ}\text{C}.$  The alkaline material is preferably in the form of solid particles or as solutions having concentrations of 5 to 50%.

In summary, in the first embodiment the treating agent Z—R attacks the calcium and/or magnesium cross-links of the tobacco protopectin and forms a precipitate which is a salt of calcium and/or magnesium, thus removing the calcium and/or magnesium cross-links from the tobacco protopectin and from the solution. In the second embodiment, the treating agent Z—R is a sequestering agent which forms a complex or chelate of the magnesium and/or calcium from the tobacco protopectin and makes the calcium and/or magnesium unavailable for recombining with the pectins. In the third embodiment, the treating agent Z—R is an acid which attacks the calcium and/or magnesium cross-links of the tobacco protopectin and forms the soluble calcium and/or magnesium salts, which are then washed away from contact with the pectins.

Once the tobacco pectins have been liberated from the tobacco, they should be released from the interstices of the tobacco. That is, they are made available to the solution or suspension or, in certain instances, merely deposited on the surface of the tobacco particles. In embodiments 1 and 2, this release may be accomplished concurrently with the first step. In embodiment 3, however, as indicated above, the insoluble pectic acid resulting from the treatment should be reacted with an alkaline material before it can be released. In such event, the release may be concurrent with the addition of the alkaline material due to a washing action. In any case, additional treating liquid or water may be used to effect the release through a washing action of the treated tobacco particles.

The liberated and separated tobacco pectins can next be precipitated from the treating solution, for example by being formed into the insoluble pectic acid or into an insoluble salt of pectic acid or by the action of a water-miscible solvent, such as acetone or ethyl alcohol to cause a water-soluble salt of pectic acid to go out of solution.

In the case of tobacco pectin solutions such as solutions of sodium and potassium pectinates and/or pectates, this can be accomplished by acidifying the solution until the pectins precipitate or by adding a gelation agent, such as an alcoholic solution, preferably having a pH of from about 1 to 9 and especially from about 1 to 5. The pH of the alcoholic solution can be regulated by the addition of a mineral acid, such as HCl, to the alcohol. Although the preferred gelation agent is ethanol, any water-miscible organic solvent having up to about 10 carbon atoms may be employed, for example, a ketone, such as acetone, or a diether, such as dioxane. Water-immiscible solvents such as ether, for example ethyl ether, can be used if combined with a water-miscible solvent, such as acetone.

The tobacco pectins can be recovered by concentrating the solution or suspension in which they are present until they precipitate. This precipitate might also be characterized as an intractable mass, since the pectin solution, upon concentration, generally becomes progressively more viscous until it finally dries to leave a deposit in a glassy solid state.

A preferred preliminary step comprises washing the tobacco plant parts, which are preferably ground or cut to a relatively small size, with cold water. This water-wash serves to remove impurities which might otherwise hinder the subsequent treatments. It is particularly desirable to employ such a cold water washing step when alkali metal carbonates are employed as the reagent in the first step. Generally, sufficient water should be used during such a water-wash operation to cover all of the tobacco plant parts present. The temperature of the water may be between  $-1^{\circ}\text{C}.$  and  $100^{\circ}\text{C}.$ , but is preferably about  $20^{\circ}\text{C}.$ , and the water wash should generally continue for a period of from  $\frac{1}{2}$  to  $2\frac{1}{2}$  hours. Agitation during the wash is desirable but not necessary. After the water-wash has been completed, the water can be removed from the tobacco parts by filtration, decantation or other suitable means.

The term "tobacco pectins" as used throughout this specification means "liberated tobacco pectins" and comprehends pectins which have been freed or liberated from tobacco and are, therefore, not bound into the tobacco structure, as differentiated from the insoluble, naturally-occurring protopectins which are bound into plant cell structure. The term includes the free pectinic or pectic acid, as well as soluble salts such as the sodium, potassium, ammonium, pectates and pectinates, and insoluble salts such as the calcium and magnesium pectates and pectinates, depending on what method is employed to liberate and obtain them from the naturally occurring insoluble protopectins.

(2) The mineral ingredient. This ingredient, which is employed to provide the proper burning qualities and the proper ash to the smoking product, may comprise an alkali metal salt or an alkaline earth metal salt, for example, a calcium, sodium, potassium or magnesium salt, or a clay.

As can be seen from the preceding discussion of the film-forming ingredients, many of the materials employed as film-forming ingredients contain combined sodium, potassium, calcium or magnesium and thus may contain sufficient "mineral ingredient" for the purposes of this invention. This combined mineral, for example, a mixture of calcium pectate and potassium pectate, can be made into a tobacco substitute having satisfactory burning qualities. However, in most cases, the film-forming component will be supplemented with other minerals. In many cases it will be desirable and preferable to add water-insoluble minerals such as calcium and/or magnesium orthophosphates, pyrophosphates and polyphosphates. A particularly advantageous mineral ingredient is precipitated tricalcium phosphate (NF grade), which has been calcined at 1000°C. for three hours. These phosphates have the particular advantage of being able to release the small amounts of calcium and magnesium ions which may be necessary to extrude the compositions at the correct texture, which must be possessed by the formulation when it is cast on a steel belt or the like. This feature is especially important when the compositions do not contain fibre which ordinarily fulfills such a function. Examples of suitable alkali metal salts and alkaline earth metal salts, which, together with clays, are the preferred mineral ingredients, for use in accordance with the present invention include the following: potassium chloride, potassium sulphate, potassium phosphate, potassium nitrate, sodium chloride, sodium sulfate, sodium phosphate, potassium nitrate, calcium chloride, calcium sulphate, calcium phosphate, calcium nitrate, magnesium chloride, magnesium sulphate, magnesium phosphate, magnesium nitrate, lithium chloride, lithium sulfate and lithium nitrate. There are many clays which can also be used. Clays are mixtures of hydrated silicates of aluminium, calcium, magnesium and zinc usually with varying amounts of iron, manganese, cobalt or other heavy metals which often impart a heavy coloration. Common names of some useful clays are Kaolin, Montmorillonite, Bentonite, Attapulgite, Allophane and Illite. Usually it is desirable to use a light-coloured or white clay, and it may sometimes be found advantageous to use fired and reground clays because such treatment renders the polyvalent cations less available (i.e., soluble) and hence less likely to interfere with the performance

of the polyuronic acid constituent of the product.

A nicotine-donating ingredient is not essential but is a preferred ingredient. The nicotine may be added in any of the known ways of incorporating nicotine in tobacco. For example, it may be added *per se* to the tobacco substitute or it may be added in the form of a material which releases nicotine upon burning of the tobacco substitute. The latter method is illustrated in U.S. Patent 3,109,436, wherein the addition of a nicotine-ion exchange resin to tobacco is described. The nicotine may also be incorporated in other portions of the tobacco product, such as the filter or wrapper to accomplish the same result.

A non-essential but very preferred ingredient of the product is a plasticizer. The plasticizer is employed to provide the desired processing characteristics for the overall composition. Suitable plasticizers include certain tobacco extracts, obtained by leaching tobacco parts with water, or mixtures of solvents such as acetone, methanol or isopropanol with water, or by leaching tobacco parts in non-aqueous solvents, such as hexane, tetrachloroethylene and ethyl ether. Other plasticizing agents include monobasic, dibasic and tribasic acids, for example: lactic, malic, tartaric and citric acids. Additional plasticizers include glycerine, triethylene glycol, sorbitol, invert sugar, sucrose, oligosaccharides, triglyceride fats and oils, long chain fatty alcohols, linear paraffins, normal paraffins, paraffin waxes, beeswax, candlelilla wax, carnauba wax, sugar cane wax, maleates, citrates and corn syrup. Particularly desirable plasticizers are sodium citrate and potassium citrate. When one or more of these materials is employed, it has been found that the subjective evaluation of the taste and aroma of the smoke resulting from products incorporating the same has been favorable.

Other materials which may be included in the tobacco substitute include nicotine-containing extracts from tobacco leaf and other flavourants which add characteristics to make a desirable smoke. Such flavorants include, for example: licorice, deer tongue, flavouring oils or rum, chocolate and fruit essence.

The amounts of the essential ingredients in the products of the present invention are dictated by the types of materials used. For example, the polyuronic acid content is suitably from 20—70% of the total weight of the mixture. When a hygroscopic organic salt is used as the plasticizer, the preferred amount of polyuronic acid is about 50%. In general, the film-forming ingredient should comprise from 5 to 95% by weight of the composition.

The minerals in tobacco leaf which pro-

vide the ash in the pyrolyzed product are in the range of 18—23% of the total weight. These are primarily calcium-magnesium-potassium salts in which the calcium and magnesium salts predominate, for example, 1 mole of calcium and of magnesium to 1 mole of potassium. Calcium to potassium ratios as high as 2.5:1 and as low as 0.7:1 and even 0.45:1 by weight, have been reported, for some leaves and stems. There are no rigid limits within the general range given below for the Mg:Ca:K ratio which is desirable since the composition may vary just as there is a wide variety in natural tobacco compositions. However, in general, the mineral ingredient should comprise from 5 to 90% and preferably from 15 to 30% by weight of the compositions.

The preferred range of the plasticizer is around 25% by weight, although 15—40% may be present. However, as pointed out above, a plasticizer is merely a very preferred ingredient and can be omitted from the composition.

Nicotine, when employed, can generally comprise from 0.3 to 3% by weight of the composition.

The order in which the ingredients are added is important in that calcium salts, when employed, should be added to the film-forming ingredient at a time when the pH of the mixture is at least 5.0 in order to prevent the calcium salts from being solubilized prematurely. The pH of the mixture should be maintained above about 5.0 because at a lower pH the calcium is very soluble and causes gelling. A preferred pH range is 5.6—8.0.

When the mixture is to be cast, it can be made into a binder material having a solids content of 5.0—25.0%. In this regard, a preferred solids content is in the range of 9—15%. If the mixture is to be extruded, a much higher solids content can be used, as high as 80%. For economic reasons, it is desirable to keep the solids content high to prevent having to evaporate great amounts of water per pound of product.

A film may be cast on a steel belt or the like by a conventional casting technique to form a burnable sheet that can then be shredded for filler in a cigarette, cigar or cigarillo. The compositions may, alternatively, be extruded into a variety of shapes or may be converted by hot roll extrusion to film form.

The use of a cast film provides the more preferred mode of operation, since the film can be more readily processed and thus more readily converted into a product which closely resembles the natural tobacco leaf product. However, the composition may also be extended in fibrous or sheet form or in other shapes, all of which can be cut into pieces

of the desired size for incorporation in the tobacco product of this invention.

The filler made by variations of the range given above and cast at 9—15% solids content on a steel belt processes well on a cigarette-making machine. Its filling power resembles that of natural leaf. Its burning qualities and ash strength are good. Subjective evaluation of cigarettes made from the filler showed that it produced a desirable, non-irritating smoke, which closely resembled that of leaf tobacco.

The invention is illustrated by the following Examples.

#### EXAMPLE 1

Pectin was extracted from the midribs of burley tobacco by treating them with diammonium phosphate (DAP)—20%, based upon the dry weight of the midribs. The pH was adjusted to 7 at the beginning of the treatment and the mixture was heated at 90°C. for one hour. At the end of that time the juice was pressed from the mixture and poured into acidified acetone to obtain the gel. The gel was filtered on cheese cloth, pressed, dried and weighed. This process gave a pectin yield of about 15%. The material was granular and had the properties of a pectic acid.

The extracted pectin (9.1 g.) was used as a film former in combination with 0.3 g. potassium hydroxide, 0.5 g. ammonia in solution, to bring the pH to 5.0, and 1.4 g. calcium pyrophosphate. The calcium and potassium were used to provide good burning qualities to the film. The calcium salt was added last to prevent the pectin from gelling before the film could be formed. The mixture was extruded on to an endless belt and the resulting film was steam-dried. The film was about 5 mils thick, was opaque, and showed a good plasticity. When ignited, the film burned well, held fire well, and formed a compact white ash. The film was shredded to make cigarette filler, which was incorporated into cigarettes. The cigarettes were smoked and their burning characteristics were observed. The burning qualities were good, and the smoke had a very mild taste.

#### EXAMPLE 2

Potassium hydroxide (197.5 g.) and magnesium hydroxide (193.5 g.) were added to 18.6 kilograms of water and dispersed in a Cowles Dissolver.

Alginic acid (1135.0 g. of Kelacid, made by Kelco Company) was added to the dispersion and the mixture was further agitated. Additional water (18.6 kilograms) and the following ingredients were then put into the Dissolver,

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- like  
noget and  
blast of midrib  
at 90°C

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grams

454.0 triethylene glycol (TEG)

45.0 nicotine

57.0 bright tobacco extract (ethylene dichloride solubles) with hexane as the carrier.

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The pH of the mixture was 4.7. The solids content was 6.35%.

- 10 The material was extruded onto an endless belt, partially dried with infrared heat, and then removed from the belt. Strips 8"—10" long were cut from the film and laid out to complete the drying process. The strips were then cut into cigarette filler.
- 15 The material processed well on a cigarette-making machine.

## EXAMPLE 3

- 20 A series of formulations were prepared to determine the ratios of magnesium or calcium to potassium that would give the most effective burning characteristics to a film designed to substitute for tobacco filler in a cigarette. The binder made from each of the formulations was prepared by dispersing pectic acid and the calcium or magnesium hydroxides in hot tap water, then adding potassium hydroxide to a pH of 5.6. The mixture was heated on a steam bath, and an equilibrium pH of 6.5 was reached.

- 30 The material was cast by conventional casting procedures and either steam- or air-dried. The resulting film was shredded into cigarette filler, and made into cigarettes. The formulations and burning characteristics are given below:

- 35 a. 51.5 g. pectic acid  
7.1 g. potassium hydroxide  
3.7 g. magnesium hydroxide.

- 40 The film that was formed held fire well, the "coal" and ash did not intumesce (puff up), and a compact white ash was formed.

- 45 b. When 4.7 g. of calcium hydroxide was substituted for the magnesium hydroxide in the formula above, the same burning characteristics were observed.

- c. 51.5 g. pectic acid  
5.54 g. magnesium hydroxide  
3.16 g. potassium hydroxide.

- 50 The film prepared from this formula did not hold fire well.

- d. 51.5 g. pectic acid  
3.13 g. calcium hydroxide  
9.52 g. potassium hydroxide.

- 55 The film from this formulation held fire well, the coal and ash intumesced (puffed up), and formed a dark ash.

- e. When 2.45 g. of magnesium hydroxide

was substituted for the calcium hydroxide in formula (d) above, the same burning characteristics were observed.

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## EXAMPLE 4

Malic acid (268 g.) was dispersed in 20 litres of tap water in a Cowles Dissolver. The dispersion was neutralized with 272 g. of ammonium hydroxide solution. One-thousand grams of sodium polypectate (Product 6024, "Sunkist" [Registered Trade Mark] Growers) was added in the Cowles Dissolver and the mixture was agitated thoroughly. Twenty grams of nicotine, 50 g. of tobacco extract (ethylene dichloride extractables from bright tobacco leaf), and 208 g. of tricalcium phosphate were added in the order named. Colouring material was added to simulate the colour of cured tobacco leaf. The colours used were F, D and C dyes—No. 1 blue, No. 6 yellow, No. 2 red and No. 5 yellow. The resulting binder material had an equilibrium pH of 6.8. The binder was extruded on to an endless belt in a layer approximately 60 mils thick, dried with infrared heat, and then stripped from the belt with a doctor knife. The film, which was leathery and flexible with a wrinkled surface, was quite similar in feel and appearance to tobacco leaf.

The film was cut into 8"×12" sheets and allowed to equilibrate to 12% moisture. The sheets were then shredded into cigarette filler by making 25 cuts/inch. The filler was made into non-filter cigarettes on a "Hauni" [Registered Trade Mark] cigarette maker. The filler processed well as compared with regular cigarette filler from tobacco.

The cigarettes were tested for resistance-to-draw (RTD). RTD is defined as the pressure drop across a cigarette, expressed as inches of water when air flows through the cigarette at a velocity of 1050 ml/min. To determine this pressure difference one end of the cigarette was inserted into a specially designed tube through which air was drawn. The pressure difference between the open and enclosed ends of the cigarette was measured. A cigarette of the present invention was found, for comparison, to be about 25% lower than that of a commercial cigarette made from tobacco but was not so low that the cigarette did not perform sufficiently well.

The test cigarettes were weighed on an analytical balance in groups of forty cigarettes and the weights of the individual cigarettes were calculated and compared with the weight of the control. The test cigarette was slightly lower in weight than the control.

The test and control cigarettes were smoked on a constant volume smoking machine which takes a 35 ml. puff of two seconds duration once in 60 seconds. The smoke was trapped on a "Cambridge" [Registered Trade Mark]

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filter pad which retains particles larger than 0.3 micron. The filter assembly was weighed before and after smoking four of each of the types of cigarettes to determine the amount of total particulate matter (TPM) collected. The TPM from the test cigarette was 12.5 mg/cigt., about half that from the control.

To determine the total alkaloid content of the test and control cigarettes, the filler was steam distilled to remove the steam-volatile alkaloids. The distillate was then used in a spectrophotometric determination. The ultraviolet absorption spectrum of the distillate was compared with appropriate standards and, with this comparison as the basis, a quantitative estimate of the total alkaloids was made. The total alkaloid content of the test cigarette compared favorably with that of the control.

The puff count for the test and control cigarette was determined by smoking four cigarettes, counting the number of puffs it took for the char line to reach the 30 mm. mark on the cigarettes, and then by taking the average of the number of puffs as the count for the individual cigarette. The puff count for the test cigarette was 13.2 and for the control, 8.0.

Forty test cigarettes were smoked on a smoking machine as described above and the particulate phase was collected on "Cambridge" filter pads. The pads were then extracted with methanol and the material was used to estimate the amount of benzo(a)pyrene in the smoke as compared with that from an all-bright tobacco cigarette which was run as a control.

The methanol-extract was evaporated on a steam bath to 3-4 ml. and enough silica gel (3-4 g.) to absorb the solution was added. The silica gel was freed of methanol in a stream of nitrogen and was added to the top of a previously prepared 25 x 600 mm. column containing 40 g. of silica gel packed as a slurry in hexane. The whole column was first eluted with 400 ml. of hexane to remove waxes. It was then eluted with benzene and the first 130 ml. of eluate after the benzene front reached the bottom of the column was collected.

The benzene eluate was evaporated to dryness and the residue, taken up in a few drops of benzene, was applied to acetylated paper in a one-inch streak. The paper was developed ascending for 16 hours with methyl cellosolve. After development, the benzo(a)pyrene zone appeared under illumination with an ultra-violet lamp as a purple fluorescent spot against a bluish-white background,  $R_f$ —0.3. The spot was excised and cut into small pieces, which were placed in a small vial and covered with 5.0 ml. of benzene-methanol, (4:1). After one hour the solvent was decanted and its fluorescence emission

spectrum was measured on a Aminco-Keirs Spectrophosphorimeter, using an excitation wavelength of 385 mμ. The amount of benzo(a)pyrene was determined by comparing the height of the 405 mμ emission band with a calibration curve obtained from standard benzo(a)pyrene solutions. The delivery of benzo(a)pyrene from the cigarette of all-bright tobacco was 0.8 parts/million. The delivery from the test cigarette was 0.45 parts/million, a reduction of almost half.

The cigarette was smoked by a smoking panel and rated in comparison with commercially available standard cigarettes. The panel found that the smoke from the test cigarette was remarkably free of harsh notes. It was deemed better than acceptable since many panel members preferred it over the control, a standard cigarette.

#### EXAMPLE 5

Seven hundred and fifty grams of sodium polypectate fortified with 250 g. of polygalacturonic acid ("Sunkist" product) were dispersed in five gallons of tap water by agitating the mixture in a Cowles Dissolver. The materials listed below were added to this dispersion:

111.0 g. calcium pyrophosphate	
21.00 g. nicotine	
53.00 g. tobacco extract (ethylene di-chloride solubles)	95
200.00 g. triethylene glycol (TEG)	
43.00 g. concentrate ammonia.	

The materials were added in a specific order. The calcium pyrophosphate was added first and then the tobacco extract which had been put in the TEG. Nicotine was added to the mixture at pH 3.5-4.0. Finally, the concentrated ammonia raised the pH to 5.0-5.5. This order of addition produced a binder-type product with a solids content of 6.3%. Colouring material was added to simulate the colour of tobacco, in the same manner as in Example 4.

The material was extruded on to an endless belt in a layer approximately 60 mils thick. The film was partially dried with infrared heat, removed from the belt and laid out in the air to complete drying. The dried film was about 6 mils thick, was pliable, and had a dull surface. The film was cut into sheets and allowed to equilibrate to 12% moisture. The sheets were then shredded into cigarette filler. They shredded well without forming undesirable quantities of dust. Cigarettes were made on the "Hauni" cigarette maker.

When the cigarettes were tested for RTD and weighed as described in Example 1, it was found that the RTD was 0.7-0.9 inches of water and that their average weight was 1.10 grams.

The test cigarettes and a commercially

70

75

80

85

90

95

100

105

110

115

120

125



available cigarette used as a control were smoked on a constant volume smoking machine, the smoke was trapped, and the TPM determined as described in Example 1. The TPM from the test cigarette was about 50% of that from the control.

The puff count for the test cigarette and control was determined as described in Example 1. The count was slightly higher than that for the control.

The benzo (a) pyrene content of the smoke from the test cigarette was determined as described in Example 1 and compared with that from a control cigarette made from all-bright tobacco. The test cigarette had a benzo (a) pyrene content greatly reduced over that of the control.

The members of a smoking panel judged the cigarette subjectively and found the smoke mild and desirable.

#### EXAMPLE 6

Seven hundred grams of sodium polypectate was dispersed as described in Example 1. The ingredients listed below were added as described in Example 2.

350.0 g. sucrose  
157.5 g. calcium pyrophosphate  
210.0 g. triethylene glycol  
14.0 g. nicotine  
35.0 g. tobacco extract (ethylene dichloride solubles)  
14 liters tap water

The equilibrium pH was 6.8.

This mixture was cast on an endless belt and partially dried with infrared heat. The film was removed from the belt with a doctor knife and dried further by air drying. The film was then cut into sheets and allowed to equilibrate to 12% moisture.

They were shredded into cigarette filler and used to prepare cigarettes.

The RTD of the cigarettes, determined as described in Example 1, was 0.9—1.0 inches of water. Their weight was about 75% that of standard cigarettes used as a control.

The TPM, determined as described in Example 1, was 31.1 mg/cigt. This was higher than the control which had a TPM of 21.8 mg/cigt.

The puff count, for the test cigarette, obtained as described in Example 1, was 11.3. The control had a puff count of 8.

The benzo (a) pyrene delivery of the test and control cigarettes (an all-bright tobacco cigarette), as determined chromatographically by the procedure given in Example 1, was 0.35 parts/million and 0.8 parts/million, respectively.

The test and control cigarettes were smoked by a test panel. The smoke from the test cigarette was judged mild and pleasing. It

had a slightly sweet taste and an aroma reminiscent of caramelized sugar.

While we do not wish to be bound by any particular theory, we believe that the sheet-forming material results in a desirable product because of the unique chemical and stereochemical properties of the natural pectic substances, algin and the like.

The pectins and algin are acids by virtue of the carboxyl groups attached at the 5th carbon position of their monomer units, whereas cellulose or hemicelluloses contain primary alcohol groupings, or methyl groups or hydrogen at this point. The carboxyl group is more readily attacked during low temperature pyrolysis than the corresponding groups of cellulose and hemicellulose; it also offers the possibility of combining ash producing cations and carbohydrate material into a single molecule.

The usual synthetic oxy-celluloses carry a partial complement of carboxyl groups at C<sub>5</sub>, but retain some unchanged cellulose units, and other cellulose units in various states of oxidation and randomly esterified by nitrogen oxides. Thus, pectins are constitutionally different from competitive smoke-producing carbohydrate materials. They are also unique and different with respect to some specific stereochemical configurations which are known to produce large differences in response to pyrolysis. The pectins (in common with starch) possess an *alpha* structure at the C<sub>1</sub> carbon, while cellulose, hemicellulose, or oxycellulose have a *beta* structure at the C<sub>1</sub> carbon. That this difference is a very large one with respect to pyrolysis may be seen by comparing the different responses of starch and cellulose to pyrolysis. Starch forms low-temperature pyrolysis intermediates; i.e. thermal starch dextrans, with which a large area of starch technology is concerned; whereas cellulose decomposes at much higher temperatures without forming any similar materials.

The pectins are also different from starch or celluloses by reason of the different configurational arrangement at the C<sub>4</sub> carbon which gives the pectin polymer "*trans*" rather than the "*cis*" configurations which is found in starch. Thus, while the *alpha* configuration leads uniquely to a "*cis*" starch polymer, the same configuration leads to "*trans*" polymer structure in the case of pectins. Other relationships are evident from the following formulas which show the structural relationships of pertinent monomer units and polymers:



$\alpha$  D Glucose  
(starch)

120

 $\beta$  D Glucose

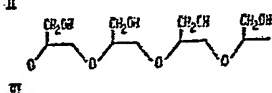
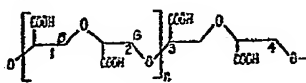
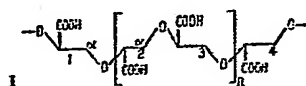
(cellulose, xylan, oxidized cellulose where  $\text{CH}_2\text{OH}$  becomes  $\text{COOH}$ )



(pectins where  $\text{CH}_2\text{OH}$  becomes  $\text{COOH}$ )  
 $\alpha$  D Galactose

 $\beta$  D Galactose

10 Where - - - is below the plane of the paper, and — is above the plane of the paper.



15 I is pectic acid (poly galacturonic) (*Alpha* configuration, galactose)

II is poly glucuronic; xylan  $\text{COOH}=\text{H}$  (*Beta* configuration glucose) cellulose  $\text{COOH}=\text{CH}_2\text{OH}$

20 where III is starch (*Alpha* configuration, glucose).

It will be seen that the algin have *beta* configurations at  $\text{C}_1$ , but because of the configurations of the mannuronic and glucuronic units, they have "trans" polymer structure.

#### WHAT WE CLAIM IS:—

1. A product for smoking in the form of a cigarette, cigar or cigarillo which contains no tobacco plant parts and which comprises a mixture of from 5 to 95% by weight of a film-forming ingredient which is an acid gum having an acid value exceeding 30 mg.

of potassium hydroxide per gram of gum, and from 5 to 90% by weight of a mineral ingredient, the balance if any, consisting of compatible ingredients.

2. A product according to claim 1 wherein the film-forming ingredient is a pectinaceous material.

3. A product according to claim 2 wherein the film-forming ingredient is one obtained by contacting tobacco plant parts with a reagent to destroy the alkaline earth metal cross-links therein, at least partially releasing the resulting tobacco pectins from the tobacco plant parts and recovering the tobacco pectins.

4. A product according to claim 3 wherein the reagent is sodium potassium or lithium carbonate, ammonium or sodium orthophosphate, or ammonium acid phosphate.

5. A product according to claim 3 wherein the reagent is a sequestering agent capable of forming a complex or chelate with the alkaline earth metal.

6. A product according to claim 3 wherein the reagent is an acid having water-soluble calcium and magnesium salts.

7. A product according to any one of claims 3 to 6 wherein the tobacco pectins are recovered by precipitation, by acidification or by adding a gelation agent.

8. A product according to claim 1 wherein the film-forming ingredient is an alginic material.

9. A product according to any one of the preceding claims wherein the mineral ingredient is an alkali metal, or alkaline earth metal, salt or a clay.

10. A product according to any one of the preceding claims which contains 20 to 70% by weight of the film-forming ingredient.

11. A product according to any one of the preceding claims which contains 15 to 30% by weight of the mineral ingredient.

12. A product according to any one of the preceding claims which contains a nicotine-donating ingredient.

13. A product according to claim 12 which contains 0.3 to 3% by weight of a nicotine-donating ingredient.

14. A product according to any one of the preceding claims which contains a plasticiser.

15. A product according to claim 14 which contains 15 to 40% by weight of a plasticiser.

16. A product according to any one of the preceding claims which contains a flavouring agent.

17. A product according to claim 1 substantially as hereinbefore described.

18. A product according to claim 1 substantially as described in any one of the Examples.

19. A burnable sheet which contains no tobacco plant parts and which comprises a mixture of from 5 to 95% by weight of a film-forming ingredient which is an acid gum

5 having an acid value exceeding 30 mg. of potassium hydroxide per gram of gum, and from 5 to 90% by weight of a mineral ingredient which is an alkali metal or alkaline earth metal salt or a clay, the balance, if any, consisting of compatible ingredients.

20. A sheet according to claim 19 having one or more of the features defined in any one of claims 2 to 8 and 10 to 16.

21. A burnable sheet according to Claim 10 19 substantially as hereinbefore described.

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